I.

A STUDY OF SOME NEW SEMIPERMEABLE MEMBRANES

II.

EXPERIMENTS ON THE PREPARATION OF POROUS CUPS SUITABLE FOR THE MEASUREMENT OF OSMOTIC PRESSURE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

ELLIOT SNELL HALL

BALTIMORE, MD.
1904

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ACKNOWLEDGMENT.

To Professor Morse, for his kindly instruction both in laboratory and lecture room, the writer desires to express his sincere gratitude.

He would also acknowledge his great indebtedness to President Remsen, Professor Renouf, Professor Jones, Professor Shattuck and Doctor Frazer.

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INTRODUCTION.

The study of osmotic pressure which was begun in this laboratory by Morse and Horn in 1901, has been continued by Morse and Frazer and others in the face of difficulties much more numerous and more serious than were anticipated at the outset.

With the discovery of a new and simple method for the preparation of an efficient semipermeable membrane came the necessity for a suitable support for the septum and a device for the accurate measurement of the high pressures developed within the cell.

In 1901, Morse and Horn[1] showed that a strong membrane could be deposited upon or within the walls of a porous clay cup much more easily and with greater certainty by electrolysis than by the diffusion method of Pfeffer. They measured pressures of not more than 4.5 atmospheres, but there was no indication that the limiting strength of the membrane had been reached at this point. It was apparent, however, that the measurement of still greater pressures was dependent upon some more effectual means of attaching the manometers to the cups.

In view of the very high pressures which were subsequently obtained, a satisfactory solution of this problem proved to be very difficult, but it was accomplished in the following year by Morse and Frazer,[2] who, after repeated failures, devised an apparatus which has withstood a pressure of more than thirty-one atmospheres and which promises to be equal to any strain which the cells themselves will bear.

The same authors also undertook a more careful investigation of the cups in the walls of which the membranes were de-

[1] *Amer. Chem. Jour.*, **26**, 80.

[2] *Amer. Chem. Jour.*, **28**, 1.

posited and made numerous observations on the measurement of osmotic pressures of half normal and normal solutions of cane sugar. They expressly state, however, that these observations "have thus far been made with reference to the testing of the construction of our cells and the efficiency of the membranes prepared by the electrolytic process and not with a view to the accurate determination of the pressures of such solutions."

Before these accurate determinations could be made it was necessary to perfect the porous cup which served as a support for the membrane.

In the meantime, another important phase of the subject was investigated. Morse and Horn, and Morse and Frazer had used only the copper ferrocyanide membrane. There was no reason to suppose that a large number of different membranes might not be found, the varying chemical properties of which might make possible the study of osmotic pressures of a much greater variety of substances than would otherwise be practicable.

Part I. of this dissertation deals with an investigation of these membranes.

It has already been mentioned that one of the most difficult problems to be solved was a method for securing the manometer in the cell. Another problem, one which has been beset with obstacles on every hand, is the preparation of a porous cup which can be relied upon to satisfy the following requirements:

1. The cup must be very strong. Morse and Frazer, working with a normal solution of sugar, measured pressures of about 471 pounds to the square inch, and there is reason to believe that even greater pressures would have been developed had not the apparatus been shattered at this point.

2. The cup must be made of very finely divided materials. Microscopic examination of cross-sections of cells has shown that those having the finest pores are those which have given the most satisfactory results.

3. The walls of the cup must be free from "air-blisters"

and cavities. It is obvious that at the point where a membrane bridges one of these cavities, it finds no support and even if it offers considerable resistance to the electric current used in the process of its formation, it cannot be expected to withstand such enormous pressures as those already mentioned.

After unavailing efforts to obtain from potteries in Boston and Baltimore, cups which would satisfy these requirements, the work of making them in this laboratory was undertaken, and has been carried on since the spring of 1903.

Part II. of this dissertation gives an account of numerous attempts made since October 1, 1903, to prepare cups which would be free from the defects of those previously used.

I. A STUDY OF SOME NEW SEMIPERMEABLE MEMBRANES.

Cells.

In the investigation[1] of the new membranes, two kinds of porous cups were used: first, bottle-shaped cups of from 175 to 200 cc. capacity, and secondly, small hard-burned cups such as had been employed by Morse and Frazer. These had an effective capacity of about 20 cc.

The walls of the bottle-shaped cells afforded such a poor support for the membranes deposited upon them that even if the cells themselves had not been deficient in strength, no very high pressures could have been developed within these cups, without rupture to the membrane.

They did, however, afford a large surface for the deposition of the membrane, and hence made it possible to test the activity of the latter by measuring the rate at which a sugar solution was delivered from the cup when the latter was immersed in pure water.

These larger vessels were not at all uniform in quality, and when broken, revealed in almost every case the presence of pores and air-blisters, sometimes as large as the head of a pin. There is also good reason for believing that the effective area varied from cell to cell, that is, that certain portions of the wall were not porous, and hence diminished the rate of endosmose of the solvent to a corresponding degree.

On account of this lack of uniformity in the texture and porosity of the cell wall, it was never safe to condemn a membrane as worthless until it had been tried repeatedly in different cells, and even then its failure to show activity or its inferiority to other membranes of different composition, might be

[1] B. F. Carver, Dissertation, Johns Hopkins University (1903); J. P. Coony, Dissertation, Johns Hopkins University (1903).

attributed to imperfections in the cell quite as justly as to the faulty nature of the septum.

While, therefore, no final conclusions as to the relative excellence of the membranes can be drawn from the experiments which are described in the following pages, this investigation may afford a basis for future quantitative work which will be made possible by the acquisition of satisfactory cells.

Solutions used in the Formation of Membranes.

Unless otherwise stated, the solutions used in the preparation of the various membranes were one-tenth normal, when first made up. Of course, where the electrodes were of platinum, the strength of the solutions in which they were immersed became constantly less. The solution around the cathode was frequently renewed in order to prevent the accumulation of alkali.

The potassium ferrocyanide employed was recrystallized several times from the commercial product. The cobalticyanide was prepared from cobalt nitrate and potassium cyanide and was also purified by recrystallization. The other salts used in the preparation of the various solutions were taken from the regular laboratory supply.

Electrodes.

Wherever practicable, the anode was of the same metal as that of the salt in which it was immersed, but in most cases both anode and cathode were of platinum. The outer electrode, which was large enough to surround the cup without touching it, was usually made the anode; the other was about 5 cm. in length and was placed within the cell.

Removal of Air from the Cell Wall.

The air was removed from the cell wall by the method of Morse and Horn, which is briefly as follows.

The cell was filled with a dilute solution of potassium sulphate and, surrounded by the platinum anode, was placed in a

beaker containing a sufficient quantity of the same solution to cover the cell. The cathode was inserted and a 110-volt current passed until from 200 to 500 cc. of the solution had been forced by endosmose through the porous walls, in the direction of the current. The form of apparatus which was used is given in detail below where the method of depositing the membrane is described.

The cell was next removed from the solution and emptied, and after washing within and without with distilled water was set up as before, except that pure water was used now in place of the sulphate solution. The current was then passed until the high resistance indicated the almost complete removal of the salt from the walls of the cell. If the membrane was not immediately deposited, the cell was kept in distilled water until required for use.

The Deposition of the Membrane.

The inside surface of the neck of the cell was first coated with shellac to prevent the formation of a membrane where it would be in danger of rupture when the stopper was removed. The cell was then fitted with a rubber stopper through which passed one end of the cross-arm of a T tube. The stem of the tube served as a horizontal outlet for the liquid which flows into the cell as a result of endosmose when the electrical connections are established.

Through the vertical portion of the T tube passed both the platinum wire which was welded to the inner electrode, and a piece of glass tubing which reached to the bottom of the cell and was attached to a funnel of convenient size at the upper end.

Through this tube the inner electrolyte was introduced from time to time, while the membrane was being deposited. This precaution was necessary in the case of membranes which were decomposed by the alkali which accumulated around the cathode.

The cell was then filled with the potassium sulphate solution

already mentioned and placed within the larger cylindrical electrode in a beaker also filled with the sulphate solution. Connection was established with the storage battery or dynamo in such a way that the current passed from the outer to the inner solution.

After the air and the potassium sulphate had been removed from the cell wall, the latter was ready for the deposition of the membrane.

The electrodes were connected with the battery terminals and the two solutions of the membrane-forming salts were poured, as nearly simultaneously as possible, the one into the beaker and the other into the cell.

An initial electromotive force of about 12 volts was usually employed. This was increased gradually, in some cases to 110 volts, in others to a smaller number, depending upon the strength of the membrane.

At first the resistance was large, owing to the presence of water in the cell wall, but as the electrolytes began to fill the pores, the current increased until the membrane began to form. At this point the resistance began to increase, attaining a maximum in anywhere from about one to five hours. When this was reached the circuit was broken and the cell was removed, washed and immersed in distilled water where it was kept until the activity of the membrane was tested.

Methods of Measuring the Activity of the Membranes.

The activity of the membranes was tested in two ways. The first of these was used only with the small cups; the second, exclusively with the bottle-shaped cells.

1. The cell was closed with a perforated rubber stopper through which passed a glass tube 4 or 5 mm. in diameter and about 75 mm. in length. Into the end of this tube a second perforated rubber stopper was fitted and through the latter a length of capillary glass tubing was passed until its lower

end was flush with the bottom of the stopper. The cell, having been previously filled with a sugar solution, was immersed in water and the height to which the solution rose in the capillary tube was measured.

2. The cell was filled with a sugar solution and closed with a perforated rubber stopper through which passed one end of a small glass tube bent to two right angles. The outer or free end of the tube was cut off at such a point that it was always above the level of the liquid in which the cup was immersed, thus preventing the formation of a siphon. As water passed in through the walls of the cell, a corresponding volume of the sugar solution was forced out through the delivery tube and was received in a 100 cc. measuring cylinder.

In the later experiments gas measuring tubes graduated to fifths of a cubic centimeter were substituted for the cylinders.

Membranes.[1]

The following membranes were investigated with regard to their activity: Uranyl phosphate, potassium diuranate, stannous hydroxide, the cobalticyanides of silver, manganese, zinc, and cadmium; the ferrocyanides of mercury, silver, tin, and uranyl. An attempt was made to prepare membranes of stannous and nickel ferricyanide, but in both cases the ferricyanide was found to be reduced and the cells were never tested for osmotic pressure.

Uranyl Phosphate.

This substance is precipitated by disodium phosphate from a solution of uranyl acetate, as a pale yellow, gelatinous mass which is easily soluble in dilute hydrochloric acid, but insoluble in dilute acetic acid.

[1] Morse and Coony have prepared the following semipermeable membranes by the electrolytic method: ferric hydroxide, ferric phosphate, the ferrocyanides of manganese and cobalt, and Prussian blue.

Morse and Carver have, by the same method, prepared membranes of the phosphates of calcium and copper, the ferrocyanides of cadmium and nickel, the sulphide of cadmium and the cobalticyanides of cobalt, nickel, copper, and iron. For details concerning these membranes vide the dissertations of J. P. Coony (1903), and B. F. Carver (1903).

The uranyl phosphate membrane was deposited in one of the small cups which for the purpose was immersed in a solution of uranyl acetate and filled with a disodium phosphate solution. The current was passed from the outer to the inner electrode.

The initial electromotive force was twelve volts. This was increased gradually until, in fifty minutes, with a voltage of 110, the resistance had reached 2,000 ohms. In three hours and twenty minutes it had risen to 6,500 ohms.

The cell was filled with an approximately half normal sugar solution, and set up with an open manometer, in the manner already described. No pressure was obtained.

The cell was removed from the uranyl acetate solution and emptied, and after being rinsed both within and without with distilled water, was subjected again to the membrane-forming process in exactly the same manner as that already described. For the sake of convenience this process will hereafter be referred to as the "reënforcement" of the membrane.

With an electromotive force of 110 volts, the resistance rose during the first forty-five minutes to 10,000 ohms, but when tested a second time the membrane gave no evidence of activity. The cup was broken and found to contain a yellow membrane of the phosphate just beneath the interior surface of the cell wall.

Another membrane of identical composition was deposited in a fresh cell of the same type. The initial voltage of the current, 10.5, was raised during the course of the first hour and a half to 111. At the end of this period the resistance amounted to 2,900 ohms and afterwards rose to a maximum of 4,900 ohms.

The cell was set up as before and this time the membrane proved to be active.

The observations which were made during the first five days of its activity are recorded in Table I. The last column gives the height of the meniscus in the capillary tube, above the water in which the cell was immersed.

TABLE I.

Dec. 15,	5 : 10 p. m.	50 mm.
" "	10 : 10	238
" 16,	3 : 30	393
" 17,	4 : 35	623
" 20,	3 : 30	889

As the cell was set up in a room which was not heated at night, it must have been subjected to changes of temperature amounting to 12° or 15° during each period of twenty-four hours.

Although allowed to stand undisturbed for two weeks, the cell never developed a pressure greater than that recorded on December 20.

When the cup was broken, the membrane was found to be situated about one millimeter from the interior and two millimeters from the exterior, surface of the cell wall, and as far as could be judged from its appearance, was as perfect as very much more active membranes of different composition prepared at a subsequent date.

As far as tested in this laboratory, membranes consisting of calcium,[1] copper[2] and ferric phosphate[3] have proved to be very much less active than would be expected from a consideration of the gelatinous character of these substances when precipitated from solutions.

There are theoretical reasons[4] for believing that if the membrane had been deposited directly upon the inner surface of the cell instead of within the cell wall, the rate of endosmose of the water, and possibly the final pressure, would have been increased.

Since the experiment described above was made, the question of position of membrane has been investigated in this laboratory by Dr. Coony, who has shown that the relative concentra-

[1] B. F. Carver, Dissertation, Johns Hopkins University (1903), p. 13.
[2] *Ibid.*, p. 14.
[3] J. P. Coony, Dissertation, Johns Hopkins University (1903), p. 16.
[4] *Ibid.*, p. 10.

tions of the electrolytes used in the formation of the membrane are the determining factors in the case. "By using high relative concentrations within [the cell] the precipitate can be formed even in the outer electrolyte and vice versa [and hence] the matter of position is under complete control."[1]

Potassium Diuranate.

When a uranyl salt is treated with caustic potash, a gelatinous, yellow precipitate is formed which is a derivative, not of the normal hydroxide $UO_2(OH)_2$, but of its anhydride

$$\begin{matrix} UO_2(OH) \\ UO_2(OH) \end{matrix} \!\!\rangle O.$$

The composition of the membrane investigated is expressed by the formula $\begin{matrix} UO_2(OK) \\ UO_2(OK) \end{matrix} \!\!\rangle O$.

Nearly all of the membranes studied in this laboratory which have given the most satisfactory results have been those formed upon the interior surface of the cell. From a consideration of the high atomic weight of uranium, it seemed probable that the uranyl ion would move much more slowly than the hydroxyl ion of the caustic potash, and that the solution of the alkali should, therefore, surround the cell which was filled with the uranyl acetate. The electrode within the cup would then be made the anode.

A small cell was accordingly filled with a tenth normal solution of uranyl acetate and immersed in a hundredth normal solution of caustic potash. With an electromotive force of twelve volts the resistance rose in twenty minutes to 600 ohms. The voltage was then increased to 46, but as the membrane showed signs of being ruptured it was reduced to 34 and fifteen minutes later to 18.5. The resistance at this time was 438 ohms, and as it fell during the next twenty minutes to 325, the circuit was broken and the cell removed for examination. Its exterior surface was found to be covered with a yellow,

[1] J. P. Coony, Dissertation, Johns Hopkins University (1903), p. 11.

rather granular precipitate unevenly distributed and, for the most part, quite easily detachable. The cell was, accordingly, prepared for a second trial by dissolving the precipitate in acetic acid which was forced through the cell wall by means of a 110-volt current. The high resistance which was finally developed indicated the almost complete removal of the acid.

The cell was then filled with a hundredth normal solution of the alkali and immersed in a tenth normal solution of the uranyl salt into which the anode dipped. The usual initial voltage of 12 was increased at the end of the first half hour to 20, where it remained for two hours and twenty minutes. The resistance reached 625 ohms. During the next two hours and forty minutes the electromotive force was raised to 57.5 volts, but as the resistance began to decrease, the cup was removed, washed, filled with strong alcohol and immersed in water. As no indication of osmotic pressure was manifest on the following morning, the stopper was removed and the interior of the cup was examined. The precipitate, as in the previous case, was granular and could be easily removed from the upper half of the cell by rubbing with the finger.

The membrane seems to be weak. In another trial with a different cup, the precipitate was formed within the cell wall instead of on its surface and yet in spite of the support which it received in this case, the resistance decreased from 4,570 to 3,086 ohms when the electromotive force was raised from 96 to 108 volts.

On account of the unpromising character of the diuranate precipitate, a more thorough investigation of the phenomena which have been described above was not undertaken. It is, however, not impossible that under different conditions the membrane may be deposited in a satisfactory manner.

Stannous Hydroxide.

When a solution of stannous chloride slightly acidified with hydrochloric acid is treated with caustic potash, a white, floc-

culent precipitate is formed which dissolves in excess of the alkali. This precipitate is stannous hydroxide.

Since the chloride of tin was used for the deposition of this substance, a platinum anode was out of the question and was substituted by one made of pure sheet tin, large enough to surround the bottle-shaped cell in the walls of which the membrane was deposited. The alkali used was caustic potash.

The initial electromotive force of 14 volts was increased during two hours to 60; the resistance rose to 220 ohms.

On the following day an attempt was made by reënforcement, to obtain a membrane which would withstand a higher voltage. The maximum resistance of 511 ohms was obtained by using a current having an electromotive force of less than 60 volts.

The membrane manifested no signs of osmotic activity.

A week later the cell was subjected to a repetition of the same treatment except that the voltage of the current was larger, ranging from 95 to 105. That this electromotive force was too high was shown by the fact that at the end of two hours the resistance was only 269 ohms.

The results were more encouraging when the cell was set up with a sugar solution in the usual manner, but the rate of delivery was so slow that no record of it was made.

About four months later the same membrane was tried again in a fresh cell of the same type. This time the resistance increased more rapidly and in two hours had reached about 700 ohms with a current potential of 99.5 volts. This looked promising, but only until experiment proved the total failure of the membrane to show activity.

The cell was reënforced, with the development of a maximum resistance of 1,530 ohms, the electromotive force of the current being 104 volts.

The readiness with which some metals form saccharates suggested the idea that previous failures with this membrane might have been due to the action of sugar upon it. Alcohol

of about 95 per cent. strength was, accordingly, substituted for the sugar and the cell was immersed as before, in water. The delivery in three days was 53.7 cc., or, in periods of twenty-four hours each, as follows: (1) 29.5 cc., (2) 18.8 cc., (3) 5.4 cc.

Silver Cobalticyanide.

Silver cobalticyanide is precipitated from a solution of silver nitrate by potassium cobalticyanide, as a white, flocculent substance which is insoluble in acetic acid but is easily decomposed by caustic potash.

One of the large cups was selected for the testing of a membrane of this composition. It was filled with a solution of the alkali cobalticyanide and immersed in a solution of silver nitrate into which the anode dipped. The initial voltage of 9 was increased during forty-five minutes to 24 where it remained for about two and one-half hours. As the maximum resistance of 74 ohms decreased during the last hour to 72 ohms, the circuit was broken and the cell was removed from the nitrate solution and emptied.

The interior surface was found to be covered with a gray precipitate consisting, probably, of the oxide of silver formed by the potassium hydroxide which collected around the cathode during the deposition of the membrane.

This accumulation of alkali can be prevented either by frequently renewing the potassium cobalticyanide solution or by adding to it a little acetic acid which neutralizes the alkali as soon as formed.

The former method having been unsuccessfully tried in the first attempt to form the membrane, the second method was employed in an effort to reënforce it. A little dilute acetic acid was added to the cobalticyanide solution in the cell, but although the resistance rose to 100 ohms, the membrane proved to be inactive.

When the cell was broken, a very regular, gray membrane was found within the cell wall.

In view of the unpromising character of this precipitate, further experimentation upon it was abandoned.

Manganese Cobalticyanide.

Manganese cobalticyanide is a white, gelatinous substance which is easily decomposed by caustic potash. For the formation of a membrane of this composition, solutions of manganese sulphate and potassium cobalticyanide were employed. One of the bottle-shaped cells containing the potassium salt was immersed in the sulphate solution which also contained the platinum anode. The initial voltage of 10 was increased to 22 an hour and a quarter after closing the circuit. Although it remained here for the next four hours the highest resistance obtainable was only 87 ohms.

In spite of the unpromising behavior of this cell, judging by the comparatively small resistance offered to the current, by the membrane, it was filled as usual with a normal solution of cane sugar and set up in the constant temperature bath which was kept at 28°. In $18\frac{3}{4}$ days the cell had delivered 105 cc.

It is quite possible that if acetic acid had been added to the cobalticyanide solution within the cup, the membrane would have proved more efficient.

Zinc Cobalticyanide.

When any soluble zinc salt is treated with a solution of potassium cobalticyanide, white, gelatinous zinc cobalticyanide is precipitated. It is soluble in the caustic alkalis but insoluble in acetic acid.

The zinc cobalticyanide membrane was, like most of the membranes already described, deposited in one of the large cups. The zinc salt employed was the sulphate and in this solution, which surrounded the cell, the zinc anode was immersed. No acetic acid was added to the potassium cobalticyanide solution in the cup.

In the first trial, the maximum resistance offered to the cur-

rent, which at no time had an electromotive force of more than 62 volts, was 392 ohms. When higher voltages were employed the membrane showed unmistakable signs of being ruptured and it was only by using great care and after passing the current for about six hours, that a membrane was built up capable of withstanding a current-pressure of even 62 volts.

The cell was filled with a normal sugar solution and immersed in water kept at 28°. The following table gives the results of observations made on the activity of this membrane. Unless otherwise indicated, the readings were made every twenty-four hours.

TABLE II.

Time.	Delivery in cc.	Time.	Delivery in cc.
12 : 10 p. m.	...	5	4.3
9 : 55 a. m.	6.0	6	4.2
1	5.5	7[1]	8.2
2	4.5	8[2]	13.3
3[1]	10.0	9	4.8
4	5.0	10	4.4

Total time of delivery 14 days, 22¼ hours.
Total volume of solution delivered, 70.2 cc.

A second trial of the same membrane was made in a fresh cup in the same manner as that just described, except that a few cubic centimeters of dilute acetic acid were added to the solution of cobalticyanide in the cell for the purpose of neutralizing the alkali which was constantly being formed at the cathode. The higher resistance offered to the current in this case is to be attributed either to this addition of acid or to the fact that the second cup was of better quality than the first.

During the course of two hours the electromotive force of the current was raised from 11.5 to 51.5 volts, where it was kept for about half an hour. The highest resistance obtained was 706 ohms.

This cell was set up in the usual manner with a normal sugar solution which was maintained at a temperature of 28°.

[1] Forty-eight hour interval between readings.

[2] Seventy-two hour interval between readings.

A record of the rate of delivery of this cell is given in Table III. Unless otherwise indicated the readings were made every twenty-four hours.

TABLE III.

Time.	Delivery in cc.	Time.	Delivery in cc.
6 : 00 p. m.	...	5	9.5
9 : 55 a. m.	9.7	6	9.5
1	8.8	7[1]	26.5
2	9.5	8	7.5
3	9.5	9	6.7
4	9.5		

Total time of delivery $11\frac{2}{3}$ days.

Total volume of solution delivered, 106.7 cc.

CADMIUM COBALTICYANIDE.

Potassium cobalticyanide precipitates from a solution of a cadmium salt, white, gelatinous cadmium cobalticyanide which is insoluble in acetic acid.

For the deposition of this membrane in one of the large cups a fifth normal solution of cadmium sulphate and a tenth normal solution of the alkali cobalticyanide were used. Both electrodes were of platinum; the outer one was made the anode, as usual. The voltage of the current was gradually increased from 10 to 52; the final resistance was 578 ohms.

The cell was filled with a normal sugar solution and set up in a bath in which a constant temperature of 35° was maintained.

Table IV. contains a record of the number of cubic centimeters delivered daily for a period of six days.

TABLE IV.

	Delivery in cc.		Delivery in cc
1	12.3	4	10.3
2	12.5	5	9.0
3	11.2	6	10.2

Total volume of solution delivered, 65.5 cc.

[1] Seventy-two hour period.

Mercurous Ferrocyanide.

An attempt was made to form a membrane of mercurous ferrocyanide in one of the bottle cells, using as the outer electrolyte a solution of mercurous nitrate to which enough of the metal was added to cover the bottom of the beaker.

The exterior electrode was, as usual, made the anode. During a period of forty minutes the electromotive force was increased from 11 to 74.5 volts, but when it was raised to 110 the resistance decreased from 784 to 733 ohms and the circuit was therefore broken.

The cell was set up in the usual manner, but as there was no evidence of osmotic pressure, it was subjected for the second time to the membrane-forming process. The current was passed for 45 minutes, practically all of this time at a voltage of 108, but although the resistance rose to 1,235 ohms, the membrane still exhibited no activity.

Only one cell was used in testing this membrane and the evidence is, therefore, not sufficient to justify the conclusion which would otherwise be drawn from the results of the experiment described above.

This membrane illustrates in a striking way the fact that the magnitude of the resistance of the membrane is not a measure of its osmotic activity.

Silver Ferrocyanide.

Silver ferrocyanide like the cobalticyanide is precipitated from silver nitrate solutions as a white, curdy mass, easily decomposed by alkalis, but insoluble in acetic acid.

A large cup was used for the testing of this substance. Before filling the cell with the ferrocyanide solution, 15 cc. of acetic acid were introduced and in every 100 cc. of the solution subsequently used there were 2 cc. of this acid.

The highest voltage employed was only 12. At one time, after the current had been passing for about half an hour, the voltage was raised to 60 but the immediate decrease in resist-

ance showed that the membrane was being ruptured, and a return was made to the original 12 volts. The membrane did not adhere to the interior surface on which it was deposited, and the resistance never rose above 86 ohms. Metallic silver was precipitated in the nitrate solution outside the cup.

The membrane gave only slight evidence of osmotic activity when the cell containing it was filled with a sugar solution and immersed in water.

While other attempts made in this laboratory to prepare an osmotically active membrane of this composition have not met with the success which might reasonably be expected from a consideration of the appearance of the precipitate, it is quite possible that under conditions as yet unknown, both the cobalticyanide and ferrocyanide of silver may prove to be suitable for the formation of semipermeable membranes.

Stannous Ferrocyanide.

Stannous ferrocyanide is precipitated as a white, flocculent substance from solutions of potassium ferrocyanide and slightly acidified stannous chloride. It is insoluble in dilute acetic acid, but is soluble in hydrochloric acid and in an excess of alkali.

The stannous ferrocyanide membrane was deposited in one of the bottle-shaped cells, the only modification in the apparatus ordinarily employed being that the large anode which surrounded the cell was of tin instead of platinum. The maximum resistance of 1,170 ohms was reached in two hours and twenty-five minutes, with a final current potential of 103 volts.

The cell was filled with a normal sugar solution and immersed in water at the temperature of the room. In 42 days the cup delivered 409 cc.

Although still active, the membrane was reënforced in the usual manner. The highest resistance obtained was 2,120 ohms, using a current with an electromotive force of 127 volts.

An attempt was then made to determine the relation at constant temperature, between the rate at which the solution was

delivered from the cell and the concentration of the sugar solution within.

The results of observations made with this end in view are presented in Table V. The temperature of the bath in which the cell was immersed was kept at 28°. Capacity of cell 186 cc.

TABLE V.

Column I. Number of cubic centimeters delivered in periods of 12 hours each.

Column II. Number of grams of sugar in 1 cc. of solution delivered.

Column III. Mean number of grams of sugar in 1 cc. solution in cell.

Column IV. Ratio of concentration of solution delivered, to mean concentration of solution in cell.

Column V. Rate of delivery in cubic centimeters per hour.

Column VI. Ratio of concentration of cell contents to rate of delivery.

	I	II	III	IV	V	VI
1	24.2	0.30054	0.32443	0.926	2.02	0.1606
2	18.0	0.26525	0.29204	0.908	1.50	0.1947
3	15.8	0.24604	0.26876	0.915	1.32	0.2036
4	14.6	0.22853	0.24934	0.917	1.22	0.2044
5	13.2	0.21267	0.23282	0.913	1.10	0.2117

Total volume of solution delivered, 85.8 cc.
Total time of delivery $2\frac{1}{2}$ days.

The figures in column II. were obtained by determining the strength of the volumes of solution given in column I. by means of Fehling's solution.

The average concentration of the cell contents during the period required for the delivery of each of these volumes, was calculated on the assumption that the membrane was impervious to a cane sugar solution, that is, that none of the sugar leaked through the walls of the cell into the surrounding water. This assumption was later proved to be incorrect and other workers[1] in this laboratory have found that membranes of other substances behave in a similar manner.

It is obvious that if the rate of delivery is proportional, at

[1] B. F. Carver, Dissertation, Johns Hopkins University (1903), pp. 21, 25, 26, etc.; J. P. Coony, Dissertation, Johns Hopkins University (1903), p. 26, *et seq.*

constant temperature, to the concentration of the solution within the cell, the ratio of the numbers representing these values should be a constant. That this is not the case, on the basis of the calculation mentioned above, can be seen from an inspection of column VI., but, as will be shown later, when the amount of sugar which leaked through the membrane was determined and the necessary correction introduced into the calculation of the strength of the cell contents, the value of the ratio approached a constant.

Column IV. gives the ratio of the concentration of the solution delivered in each period of twelve hours to the average concentration of the cell contents for the same period of time. It will be noticed that the highest value of this ratio expressed in percentages is 92.6, which means that the concentration of the delivered liquid is less by at least 7.4 per cent. than would be expected. The only obvious explanation of this fact is that the water which enters the cell through the membrane glides up the wall toward the top, giving in that region a solution which is more dilute than that in the interior portions of the liquid. Although the values of the concentrations presented in column III. are undoubtedly too high, owing to the undetermined amounts of sugar which must have leaked through the membrane, the error in the calculations arising from this source can scarcely have been great enough to account for this discrepancy of more than 7 per cent.

Data concerning this point are presented in Table VII. on page 30 and will be discussed in connection with facts brought out by a study of the uranyl ferrocyanide membrane.

Uranyl Ferrocyanide.

A brownish red precipitate of uranyl ferrocyanide is formed when a solution of uranyl acetate is treated with potassium ferrocyanide. It is insoluble in dilute acetic acid but is easily dissolved by warm dilute hydrochloric acid. It is easily decomposed by sodium and potassium hydroxide and for this

reason care must be taken to prevent an accumulation of alkali around the cathode during the deposition of the membrane. In the experiment to be described this was accomplished by frequently renewing the potassium ferrocyanide solution.

The first uranyl ferrocyanide membrane was deposited in one of the small cups which was, accordingly, immersed in a solution of uranyl acetate containing the anode and filled with a solution of potassium ferrocyanide.

The electromotive force of the current which was used at first was 29 volts. This was increased to 96 volts during the first hour and forty minutes at the end of which period the resistance was 9,600 ohms. During the next half hour the voltage was raised to 109, and the maximum resistance of 10,850 ohms was reached.

When the cell was filled with an approximately normal sugar solution and immersed in a beaker of water standing on the floor, the liquid rose in the capillary tubing to a height of about 12 feet. At this point connection was made by means of a tube bent to two right angles, with a test-tube which received the overflow. In this way about 10 cc. of the sugar solution were collected during the next few days.

The cell was broken and found to be covered on the interior surface with a membrane which did not at all resemble in color the dark red precipitate of the uranyl ferrocyanide but was pale yellow, with traces of green and blue. Since all membranes of this composition, so far as observed, suffered this change of color when allowed to stand in contact with a sugar solution, it seems probable that they are decomposed by it.

A membrane of the same composition was deposited in one of the bottle-shaped cells. The electromotive force at the beginning was 7 volts. In one and one-half hours the resistance had reached 686 ohms and about three hours later, with a voltage of 108, the maximum resistance of 1,009 ohms was obtained.

The activity of this membrane was tested according to the

second method already described, using a sugar solution which was about normal. During the first sixteen days the cell delivered 227 cc.; the total delivery in 42 days was 418 cc.

No attempt to investigate the relation between concentration and rate of delivery was possible as long as the cell was subjected to fluctuations of temperature which often amounted, during a period of twenty-four hours, to 15°.

The cell was emptied, thoroughly rinsed with water and about a week later was set up without reënforcement of the membrane, in the same manner as before, except that the water in which the cell was immersed was kept at a constant temperature of 28°. Under these conditions the cell delivered 142 cc. in nine days.

Although the membrane still showed activity it was reënforced in the manner previously explained, before it was set up for the third time. The voltage of the current was increased more rapidly than was the case when the membrane was first deposited and the current was passed for only about half an hour. During this short period of time the voltage was raised from 11 to 103 and the maximum resistance of 1,716 ohms was reached.

The results of observations made upon the osmotic activity of this membrane are presented in Table VI.

The cell, which had a capacity of 178 cc., was filled with a solution containing 279.75 grams of sugar per liter, as determined by Fehling's solution.

The bath in which the cell was placed was maintained at a temperature of 28°.

The figures in column II. were obtained from a determination, by means of the Mohr-Westphal balance, of the specific gravity of the volumes of solution given in column I.

A comparison of columns II. and III. shows that here also, as was the case in Table V., the mean concentration of the cell contents for a specified time, if the leakage of sugar was not taken into account, was always greater than the

concentration of the solution delivered during the same period of time.

TABLE VI.

Column I. Number of cubic centimeters delivered in 12-hour periods (except as otherwise indicated).

Column II. Number of grams of sugar in 1 cc. of solution delivered.

Column III. Mean number of grams of sugar in 1 cc. of solution in cell.

Column IV. Ratio of concentration of solution delivered, to mean concentration of solution in cell.

Column V. Rate of delivery in cubic centimeters per hour.

Column VI. Ratio of concentration of cell contents to rate of delivery.

	I	II.	III	IV	V	VI
1	43.0	0.22255	0.25287	0.880	3.58	0.0706
2	32.1	0.18252	0.20953	0.871	2.68	0.0782
3	27.7	0.15922	0.18068	0.881	2.31	0.0782
4	24.0	0.13911	0.15892	0.875	2.00	0.0794
5	20.7	0.12499	0.14227	0.879	1.73	0.0822
6	17.9	0.11262	0.12934	0.877	1.49	0.0865
7[1]	31.0	0.09860	0.11509	0.857	1.29	0.0892
8	13.8	0.08492	0.10321	0.823	1.15	0.0897
9	11.8	0.07879	0.09311	0.846	0.98	0.0950
10[1]	21.0	0.07336	0.09037	0.812	0.88	0.103
11[1]	17.2	0.06657	0.08283	0.804	0.72	0.115
12[1]	16.5	0.06347	0.07668	0.828	0.69	0.111

Total volume of solution delivered, 276.7 cc.

Total time of delivery, 8 days.

By an inspection of column IV., which contains the ratios of the numbers in column II. to those in column III., it will be seen that the concentration of the delivered liquid was less by at least 12 per cent. than would be expected.

It is obvious that a correction for the leakage of sugar through the membrane would reduce the values of the mean concentrations of the cell for specified times, as presented in column III., and that consequently the numbers given in column IV. would approach more nearly 100 per cent.

As was stated in the discussion of Table V., the other cause of the discrepancy between the values of the concentration of the delivered solution and the mean concentration of the cell contents, was thought to be the incomplete diffusion of the water which entered the cell.

[1] Twenty-four hour periods.

Column VI. gives the ratio of the average concentration of the cell contents for a specified time to the rate of delivery of the cell for the same period of time. Here also as was the case in Table V., the ratio does not have the constant value which it would possess if the rate of delivery were proportional to the concentration of the solution in the cell. It will further be noticed that in both Table V. and Table VI., the value of the ratio increases from the top to the bottom of the column.

This increase can be satisfactorily accounted for by a consideration of the fact that if the cell had suffered a constant decrease in concentration due to leakage of sugar through the membrane, the error produced in the calculations of the concentrations as given in column III. would be cumulative and would tend to produce the increase in the values of the ratios found in column VI.

The membrane in this cup was reënforced for the last time on April 20. The maximum resistance obtained with a current of 104 volts was 2,600 ohms.

With a view to ascertaining more exactly the average concentration of the contents of the cell for any period of time, it became necessary to determine the amount of sugar which had leaked through the membrane during this time as well as that which had been collected in the gas measuring-tube. The sum of these two quantities would be equal to the total decrease in the concentration of the cell.

The only other change which was made in this experiment consisted in the use of a stirrer which kept the liquid in the cell in constant motion. A piece of glass tubing 3 or 4 cm. in length and of about the same diameter as the neck of the cell, was provided with a horizontal side tube, the outer end of which was bent down for the delivery of the liquid into the measuring-tubes. Through the vertical tube which was joined to the neck of the cell, was passed a silver-plated steel rod, to the lower end of which were fastened two cross-pieces of platinum foil shaped like the blades of a propeller. This stirrer,

which on preliminary trial proved to be very efficient, was driven by a small electric motor.

The results of the last observations which were made in connection with this cell are presented in Table VII.

The concentration of the sugar solution used in filling the cup, as determined by Fehling's solution, was 337.9 grams per liter. The temperature of the bath in which the cell was set up ranged from 27°.7 to 31°.2. Capacity of cell with stirrer in place 194.8 cc.

TABLE VII.

Column I. Volume of delivered solution in cubic centimeters.

Column II. Number of grams of sugar in 1 cc. of solution delivered.

Column III. Mean number of grams of sugar in 1 cc. of solution in cell, (corrected for leakage).

Column IV. Ratio of concentration of solution delivered, to mean concentration of solution in cell.

Column V. Rate of delivery in cubic centimeters per hour.

Column VI. Ratio of concentration of cell contents to rate of delivery.

Column VII. Number of grams of sugar in water surrounding cell.

	I	II	III	IV	V	VI	VII
1	22.4[1]	0.30282	0.32409	0.934	3.70	0.0876	0.232
2	31.8[2]	0.24198	0.28571	0.935	2.65	0.108	0.285
3	27.3	0.23094	0.24818	0.931	2.28	0.109	0.297
4	22.3	0.20446	0.21862	0.935	1.86	0.118	0.357
5	20.7	0.17834	0.19575	0.911	1.73	0.113	0.300[5]
6	18.0	0.15931	0.17738	0.898	1.50	0.118	0.300[5]
7	17.0	0.14591	0.16119	0.905	1.41	0.114	0.489
8	15.7	0.13375	0.14597	0.916	1.31	0.111	0.519
9	39.4[3]	0.11069	0.12497	0.886	1.09	0.115	1.029
10	11.0	0.09413	0.10581	0.889	0.92	0.115	0.315
11	21.7[4]	0.08174	0.09804	0.834	0.90	0.109	0.627
12	19.5	0.06963	0.08708	0.800	0.81	0.107	0.511
13	18.6				0.77		
14	15.3				0.64		
15	14.0				0.58		
16	12.6				0.52		
17	11.9				0.50		

Total volume of solution delivered, 339.2 cc.

Total time of delivery 13¾ days.

[1] Six hour period.

[2] Cell contents not stirred.

[3] Thirty-six-hour period.

[4] (11)–(17) twenty-four-hour periods.

[5] Estimated.

Attention has already been called to the fact that according to the figures presented in column VI. of Tables V. and VI., the ratio of the average concentration of the cell for a specified period of time, to the rate of delivery for the same period, does not approach a constant but that there is, instead, a continuous increase in the value of those ratios.

The effect of a determination of the leakage of the cell is made apparent in column VI. of Table VII. With the exception of (1) these numbers approach a constant lying somewhere between 0.107 and 0.118.

The results presented in column IV. of the same table are not as satisfactory. From a consideration of the efficiency of the stirrer it seems impossible to believe that the water which constantly entered the cell was not thoroughly diffused throughout the solution within, and yet the figures seem to show that this was not the case but that, as before, the contents of the cell at any specified time was more concentrated than was to be expected. The continuous decrease in the percentages from 93.4 to 80.0 remains unexplained. Analogous cases[1] have been met with in this laboratory.

When this cup was broken, the membrane was found to be situated on the interior surface and to be of the bluish yellow color already mentioned. The membrane adhered very firmly to the cell walls.

Conclusions.

The investigation described in the preceding pages seems to justify the following conclusions:

1. That membranes may be easily deposited by the electrolytic method upon or within the walls of porous clay vessels separating solutions of two electrolytes capable of forming a precipitate.

2. That the number of semipermeable membranes capable of formation by this method is large.

3. That of the membranes investigated, the uranyl ferro-

[1] B. F. Carver, Dissertation, Johns Hopkins University, (1903), pp. 26, 35.

cyanide membrane seems to be the most promising for use in the measurement of high osmotic pressures.

4. That when cells of the form employed in this work are used, the liquid delivered during any period of time is less concentrated than the average contents of the cell during the same period.

5. That the magnitude of the electrical resistance of membranes deposited within or upon the walls of the imperfect cells at the writer's disposal, is not a measure of the osmotic activity of these membranes, or of their suitability for use in the measurement of osmotic pressure. All semi-permeable membranes consisting of precipitated chemical compounds are weak, that is, easily ruptured, and can therefore be made to serve for the measurement of high pressures only by giving them a most perfect support at all points.

A problem which has been foreseen from the very beginning of the work of Morse and Frazer is now practically the only one which prevents the prosecution of the investigation of osmotic pressure phenomena upon a quantitative basis. Until a satisfactory porous cup is procured, all reliable quantitative measurements either of the rate of endosmose of pure solvent through the membrane or of the actual pressures developed within the cell, is impossible. The direction, therefore, which future work must necessarily take, was plainly indicated, and attention was turned from the study of the membranes to the construction of suitable porous vessels in which to deposit them.

The prospects of early success in this direction are not great, but if the desired end is eventually attained, the contributions to theoretical chemistry which it will make possible will more than justify the expenditure of the time and labor which its accomplishment has cost.

II. EXPERIMENTS ON THE PREPARATION OF POROUS CUPS SUITABLE FOR THE MEASUREMENT OF OSMOTIC PRESSURE.

The three essential characteristics of cups suitable for the measurement of high pressures have already been mentioned, viz., strength, the greatest compactness and uniformity of structure compatible with the requisite porosity, freedom from cavities and air-blisters. Many of the cells obtained from the potters were satisfactory as far as the fineness of the ingredients used in their manufacture was concerned, but only a very small percentage of them approached even distantly the required standard of strength and uniform density of texture. The only remaining way of obtaining porous vessels free from these defects seemed to be to prepare them in the laboratory.

Through the courtesy of D. F. Haynes & Son, of the Chesapeake Pottery in this city, four varieties of clay were obtained from their works. These were washed by elutriation and only the finest of the material thus separated was dried and used in the preparation of the cells.

One thing seemed certain at the outset — that in the process of moulding, very much greater pressure must be employed than that commonly used in the potteries. Air-blisters or cavities which for any reason might otherwise be present, would be removed by this treatment and the density of the cell wall would be increased.

The improved condition of the air-dried vessel when it was placed in the kiln for burning, would not, however, insure the equally perfect quality of the finished product. Indeed it was thought probable that most of the cavities and channels might be formed during the process of burning, for if the chemically combined water in the clay were driven off too rapidly, that which was liberated at any point beneath the surface of the cell

wall might force its way out with such violence as to form the cavities and channels which were so often met with in the vessels obtained from the potters.

If the true cause of these defects was the rapid expulsion of the chemically combined water from the clay, then a determination of the temperature at which this reaction took place most energetically was necessary, and a furnace capable of very perfect regulation up to a somewhat higher temperature became essential.

The first requisite was a suitable apparatus for forming the cups under high pressure. The following brief description of the mould which was devised and used by Morse and Frazer will serve the present purpose. The details of its construction will be published in another place.

The Mould.

The strong iron vessel 14 cm. in diameter and 13 cm. deep, which contains the mould proper, is made of two parts symmetrically situated with reference to an imaginary vertical plane passing through the center. These parts can be securely fastened together by means of bolts on the sides. In this iron vessel the plaster of Paris mould, with the cell-shaped cavity in the center, is cast in two parts so that the plane of their surfaces of contact coincides with the vertical plane of division of the containing vessel.

Around the upper edge of the vessel extends a flat rim 2.5 cm. in width and to this an iron top can be bolted, through the center of which and hence directly above the cavity in the plaster of Paris, is a threaded hole 8 cm. in depth and about 3 cm. in diameter. A steel plunger 23 cm. in length, the lower end of which is of the exact size and shape of the interior surface of the cup, is threaded at the upper end to fit the hole and can be raised or lowered by means of a wrench.

The process of moulding the cup consists of introducing a sufficient amount of moist clay into the plaster mould, of

roughly shaping the clay in the mould with the fingers, of bolting the iron top to the vessel beneath and finally, of screwing down the plunger to a proper point by means of a long-handled wrench. The water which is pressed out of the clay is absorbed by the plaster of Paris and the cell is easily taken from the mould, after the withdrawal of the plunger and the removal of the top, by unscrewing the bolts on the sides of the iron vessel and carefully separating the two parts.

Dimensions of the Cup.

The dimensions of the cell as it leaves the mould are as follows: length 93 mm.; internal diameter at top 25 mm.; external diameter at top, including rim, 37 mm.; external diameter at top just below rim 31 mm.; external diameter at bottom 24 mm.

The Electric Furnace.

The temperature at which the three varieties of clay lost fifty per cent. of their chemically combined water was determined by means of an electric furnace and a Le Chatelier pyrometer to lie between the limits 425° and 450°. If then, the assumptions made above were in accordance with the facts, it would be necessary to raise the temperature very slowly between these limits.

Since the most perfect regulation of high temperatures is best accomplished in the electric furnace, and since the instrument hitherto employed proved to be somewhat unsatisfactory, a suitable furnace had to be devised.

In its perfected form the instrument devised in this laboratory by Morse and Frazer and described below, has proved very efficient for use up to a temperature of about 1100°. Above this point the platinum used in its construction volatilizes to such an extent that repeated heating would shorten the life of the wired portion to an unwarrantable degree.

The form and size of the furnace may be varied within very wide limits. The following is a brief description of the

one which was used in nearly all of the work which will be detailed in the following pages.

The essential parts of the furnace are: (1) an outer cylinder of sheet-iron covered both within and without with asbestos paper; (2) a smaller cylinder of fire-clay; (3) a second cylinder of fire-clay smaller than the first; (4) a wired portion which forms the center of the apparatus. This inner wired portion where the heat is generated is constructed as follows.

Three fire-clay rings are held in horizontal positions one above another by three vertical platinum rods 11 cm. in length which pass through holes in the rings and are threaded at both ends. The two lower rings are each 5 mm. in thickness; the top one is just double this amount. Each threaded portion of the rods carries two platinum nuts, three of which are directly above and three directly below the top and bottom ring respectively. Another important rôle which these rods play when the furnace is in use will be pointed out later. The third ring is situated midway between the other two rings and is fastened to the rods with platinum wire. The middle and lowest rings have the same external diameter of 6.3 cm., but the internal diameter of the lowest one is smaller, since this ring forms a support for objects to be heated in the furnace. The uppermost ring has the same internal diameter as the middle one, viz., 4.5 cm., but projects beyond the other two by an amount equal to the thickness of the smaller clay cylinder which supports it.

Each ring is perforated with a double series of concentric holes 5 mm. apart, and through these two pieces of number 26 platinum wire (B. & S. gauge), each about 3.6 meters in length, are woven up and down and across the bottom, each wire serving to wind up one half the furnace.

When the furnace is in use the three vertical rods previously mentioned are heated very nearly to the temperature of the platinum wires through which the current is passing, and consequently expand to nearly the same extent. The distance between the top and bottom rings is increased proportionally

and the wires are thus kept straight both during the heating and the cooling of the furnace. This arrangement is important, for if the wires were not straightened as they are expanded by heat there would be danger of short-circuiting the current, due to contact of two adjacent wires. These rods also serve to prevent the stretching of the wires which might take place at high temperatures if the weight of the cell which rests on the lower ring were not supported by them.

The wired portion of the furnace is suspended free in the smaller cylinder of fire-clay, previously mentioned, which is 12 cm. in height and 7.8 cm. outside diameter. The lower end of the cylinder and the upper ring are provided with closely-fitting discs of fire-clay.

The larger clay cylinder which surrounds the one just described and is separated from it by an annular air-space of 1 cm., is 16 cm. in height, 12 cm. external diameter, and about 1 cm. in thickness. This is fitted with a top and bottom like the inner cylinder. Both the outer and inner cylinders are supported, each by means of three truncated cones of fire-clay 1 cm. in height.

Surrounding all is a cylinder of sheet-iron covered with asbestos paper and provided with a top of asbestos board. This cylinder is 19.5 cm. in height and 16 cm. in diameter, and rests upon a base of heavy asbestos board beneath which is a soap-stone slab.

In the centers of the three cylinder covers are holes 1.2 cm. in diameter, through which a thermometer or the clay cylinder carrying the wires of the thermo-couple can be introduced.

A Le Chatelier pyrometer connected with a Keiser and Schmidt voltmeter was used in determining the temperature of the furnace above 300°. The voltmeter was provided with two scales, one of which was graduated to decimillivolts, the other for direct reading of the temperature. Each division of the latter scale was equivalent to 20°, so that the temperature could easily be estimated to within two or three degrees. The

thermo-couple, which had been tested at the Reichsanstalt, was a junction of platinum and platinum containing ten per cent. rhodium.

Calibration of the Electric Furnace.

The depth of the wired portion of the furnace, that is, the distance between the top and bottom rings was just sufficient for the introduction of one of the clay cups which rested on the lower ring. Since there was no room for the thermo-couple when the cell was in place, a calibration of the empty furnace became necessary, that is, the maximum temperature obtainable with a specified current had to be determined for certain points at convenient intervals up to the highest temperature required for burning the cells. The strength and voltage of the current having been determined for each point, the corresponding resistance of the furnace and the electrical energy consumed in maintaining the latter at this temperature could be calculated, and from these data, by interpolation, the resistance and disappearing electrical energy for all intermediate temperatures could be determined.

The results of the calibration are presented in Table VIII.

Table VIII.

Amperes.	Volts.	Temp.	Ohms.	Joules.
4.0	18.0	385°	4.50	72.00
4.2	19.8	420	4.71	83.16
4.4	21.3	446	4.84	93.72
4.6	23.3	481	5.07	107.18
5.4	31.2	617	5.78	168.48
5.93	36.9	742	6.22	218.82
6.53	43.6	845	6.68	284.71
6.93	48.4	904	6.98	335.41

The method of calculating the resistance for temperatures not given in the table, lying between 385° and 904° may, perhaps, be best illustrated by an example.

Suppose it is required to find the resistance of the furnace for each degree lying between 385° and 420°. The resistance for 420° was 4.71 ohms; that for 385° was 4.50 ohms. The

increase in resistance corresponding to an increase in temperature of 35° is, therefore, $4.71 - 4.50 = 0.21$ ohm, or the increase in resistance for a rise of 1° is $0.21 \div 35 = 0.006$ ohm. The value thus obtained is, for convenience, called the "resistance coefficient" for this interval of 35°. The increase in the number of joules consumed for an increase of 1° can be calculated in a similar manner. The value so obtained is termed the "energy coefficient."

The resistance for temperatures lying between 385° and 420° may, therefore, be found by adding to 4.50 ohms, the resistance at 385°, 0.006 ohm for each rise of one degree.

Table IX. shows the resistance and energy coefficients for each temperature interval given in the first column of Table VIII.

TABLE IX.

Temperatures.	Resistance Coefficient.	Energy Coefficient.
385°–420°	0.0060	0.3189
420–446	0.0050	0.4062
446–481	0.0066	0.3845
481–617	0.0052	0.4507
617–742	0.0035	0.4027
742–845	0.0045	0.6397
845–904	0.0051	0.8593

It will be seen from the data given in Table VIII. that it was possible to prepare a table containing the resistance of, and the electrical energy consumed in, the furnace, for each degree between 385° and 904°. Conversely, if the resistance and disappearing electrical energy were known, the temperatures corresponding to each could be determined by reference to the table.

An example will, perhaps, make the method of procedure more obvious. In burning one of the cells the current used at one time was 4.3 amperes when the fall in potential within the furnace was 20.2 volts. The resistance calculated from these data was found to be 4.70 ohms, and the electrical energy consumed to be 86.86 joules. By reference to the table prepared

according to the method described above, it was found that for a resistance of 4.70 ohms the temperature was 418° and for 86.86 joules it was 430°. The meaning of this discrepancy between the results obtained by the two methods of calculation is explained below.

It will be obvious from what has already been said that when the furnace had once been accurately calibrated by means of the thermo-couple, its temperature at any subsequent time could be calculated, provided only the current flowing in the circuit and the fall in potential within the furnace were both known.

Since the resistance was determined by the value of the quotient E/C, in which E represents the electromotive force and C the strength of the current, and since the number of joules of electrical energy disappearing as heat is determined by the value of the product $E \times C$, it would at first sight seem to be immaterial whether the resistance coefficient or the energy coefficient were taken as the basis for calculating the temperature of the furnace at any time. A moment's reflection will, however, be sufficient to show that these two methods would give the same result only when the electrical energy, which was continually being transformed into heat energy, was all used up in maintaining the temperature of the furnace. If this were not the case, if, for instance, some of the heat energy were spent in vaporizing water, then the energy available for maintaining the temperature of the furnace would be diminished by just this amount and the resistance of the furnace would consequently be less than would otherwise be the case. As soon, however, as all the water were vaporized, the energy available for maintaining the temperature of the furnace would be increased by an amount equal to the latent heat of vaporization of water; the temperature of the furnace would rise and the resistance would increase.

This was exactly what proved to be the case when the air-dried cells were burned. With each increase of current, the

temperature as calculated from the resistance was at first lower than that calculated from the electrical energy which was used up in the furnace, but gradually increased until the two were nearly or quite equal. When the current was raised again the same phenomenon was observed and so on to the end. It thus became possible to determine the end of the reaction which resulted in the expulsion of the chemically combined water in the clay, and to regulate the current accordingly.

In this connection, however, it must not be forgotten that a certain time is required to raise the temperature of the furnace to the maximum obtainable with any specified current, and that, consequently, even with an empty furnace, the temperature calculated from the resistance would be lower than that calculated from the disappearing electrical energy, until equilibrium were established. By measuring the time required to bring about this state of equilibrium a more correct idea could be formed of the energy changes which accompany a reaction within the furnace.

An exothermic reaction should have an effect just the opposite of the endothermic one described above; that is, the heat which is evolved when the reaction takes place must raise the temperature of the furnace and hence produce an increase in the resistance of the wires. The temperature calculated from the resistance would, in this case, be *greater* than that calculated from the amount of electrical energy consumed.

The principle involved in these phenomena seems capable of extensive application and experiments already carried out or now in progress in this laboratory justify the hope that it will contribute much to our knowledge of reactions which take place at high temperatures.

The Gas Furnace.

It has already been stated that the electric furnace could not be used advantageously at temperatures above 1100° or thereabout, owing to the volatility of the platinum. It was, how-

ever, necessary to burn the cells at about 1300°. For obtaining these higher temperatures a modified form of the Seger gas furnace was used and its temperature ascertained by means of Seger cones. The quantity of gas consumed in the production of a temperature just sufficient to soften one of the cones was measured with an ordinary twenty-light gas meter.

Table X. contains the results of some observations made on the calibration of this furnace.

TABLE X.

Cubic Feet Gas Consumed per Hour.	Temperature of Furnace.
41	(about) 800°
51	950
60	1090
71	1290

Owing to the fact that the gas pressure was never perfectly constant, the figures given in the first column represent only approximately the true values.

OBSERVATIONS ON THE BURNING OF CELLS.

With the exception of the cell VI. mentioned below, all of the cells described in the following pages were moulded under high pressure in the manner described on pages 34 and 35.

The three varieties of clay obtained from D. F. Haynes & Son for the preparation of the porous cups, are known as

TABLE XI.

	Florida Clay.	Peach Clay.	Eng. Ball Clay.
H_2O	13.35	12.28	11.91
SiO_2	46.07	48.09	49.38
Al_2O_3	38.48	35.78	35.19
Fe	.....	1.84	.....
CaO	0.24	.....	.....
MgO	0.26	Trace	.....
K_2O	1.88	2.36	2.54
Na_2O	.....	.....	.....
C	.....	0.4	.....
	100.28	100.75	99.02

Peach, Delaware; Edgar, Florida; and English Ball clay. These clays, after washing and bolting, were analyzed by Mr. L. S. Taylor, to whom the writer is indebted for the data presented in Table XI. The figures express percentages.

Cup I. — The composition of this cell was Delaware clay without the admixture of silica, feldspar or other clays. It was dried in the air for an unknown time, but certainly for thirty-six hours, before being heated in the electric furnace.

The cell was placed in the furnace at 9 a. m. on November 23. The initial current, which was not recorded, was raised very gradually, until at 4:30 p. m., it was 4.4 amperes.

Table XII. contains a few of the data obtained in burning this cup.

TABLE XII.

Time.	Amperes.	Volts.	Ohms.	Joules.	Temperature Found.	Temp. from Elec. Energy.
November 23.						
4:30 p. m.	4.42	21.1	4.77	93.26	434°	443°
7:30 "	4.40	21.4	4.86	94.16	449	450
10:30 "	4.50	22.2	4.93	99.90	461	461
November 24.						
6:00 a. m.	4.51	22.3	4.94	100.57	463	463
12:50 p. m.	4.65	23.8	5.12	110.67	487	489
5:30 "	5.00	26.8	5.36	134.00	537	540
8:30 "	5.10	27.6	5.41	140.76	548	558
November 25.						
6:30 a. m.	5.10	27.8	5.45	141.78	556	559
12:30 p. m.	5.2	29.1	5.60	151.32	582	579
6:30 "	5.6	33.2	5.93	185.92	660	660
9:00 "	6.0	37.3	6.21	223.80	743	750
9:40 "	6.0	37.5	6.26	225.00	750	752
12:00 night.	6.4	41.6	6.50	266.24	804	816
November 26.						
12:30 a. m.	6.4	41.7	6.52	266.88	808	817
1:00 "	6.4	41.8	6.53	267.52	811	818
4:05 "	6.9	47.4	6.87	327.06	882	894

The last figures in column VII. indicate the highest temperature at which the cell was burned in the electric furnace.

The current was diminished very slowly in order to lessen the danger of cracking the cell, which was removed when quite cool, and a few days later was placed in the gas furnace for

the final burning. Here also care was taken to raise the temperature slowly to the maximum which was maintained for about sixteen hours and then the supply of gas was gradually lessened until, in thirty hours from the beginning of the burning, it was shut off completely.

Highest temperature of furnace not known, but certainly below 1290°, as determined by the Seger cones. Length of cell after burning 3.58 inches. It was evident both from the moderate shrinkage of the cup and its great porosity when tested with the tongue that it had not been burned at a sufficiently high temperature. It was reburned in the gas furnace for thirty-three and one-half hours, the maximum temperature of 1270° being maintained for about ten hours.

Length of cell upon removal from furnace 3.45 inches. Shrinkage during second burning in gas furnace 3.6 per cent.

When filled with water the whole exterior surface of the cell became moist at the same time, indicating that the walls were quite uniformly porous. When the same test was applied to the bottle-shaped cells, certain areas of the walls were frequently found to be either impervious to water or at least very much less porous than other portions.

An attempt was made to deposit a membrane of copper ferrocyanide in this cell, but when the resistance had reached 4,800 ohms, it was discovered that the cell was cracked. Whether this crack was produced during the burning of the cell or by subsequent treatment, is not surely known, but the latter is believed to be the case. To those whose greatest difficulty thus far has been to prepare a suitable cell free from cracks, this apparently insignificant fact seems worthy of mention.

The vessel was broken and the fractured surfaces were examined. The walls seemed to be very free from cavities and channels, but were also deficient in strength.

Cup II. — The composition of this cup was the same as that of I, viz., Delaware clay without any admixture of other ma-

terials, and like it, was dried in the air at ordinary temperature before being placed in the electric furnace.

The initial current of 1.7 amperes was gradually increased until in eight days three and one-half hours the maximum temperature was reached. The observations made at this time were as follows: current, 6.5 amperes; electromotive force, 43 volts; resistance, 6.61 ohms; temperature calculated from resistance, 830°; electrical energy consumed in the furnace, 279.5 joules; temperature calculated from disappearing electrical energy, 836°.

The cell was next burned in the gas furnace at a maximum temperature of 1310°, the customary precaution being taken to insure the gradual raising and lowering of the temperature.

Length of cell when taken from the electric furnace 3.66 inches. Length of cell when taken from gas furnace 3.34 inches. Shrinkage of cell in gas furnace 8.7 per cent.

Although some slight cracks were visible in the walls of this cell, it was thought that some idea of its porosity and of its suitability as a support for a semipermeable membrane might be obtained by an attempt to deposit in it a membrane of copper ferrocyanide. The methods employed were essentially those which were described in Part I. of this dissertation. Instead, however, of using a small voltage at the beginning, a current at 109 volts was employed throughout the process of membrane formation. The maximum resistance of 99,400 ohms was developed in one hour. At the end of three hours the resistance had decreased to 84,000 ohms.

The cell was filled with a half normal solution of cane sugar and set up essentially in the manner described by Morse and Frazer.[1] Practically no pressure was developed within the cell.

An attempt was made to reënforce the membrane by means of a current of 109 volts which was passed for two hours. The final resistance was only 13,600 ohms and as it had been de-

[1] *Am. Chem. Jour.*, **28**, 3.

creasing from the very first, the circuit was broken and the cell was again set up with a half normal sugar solution. In nine hours a pressure of 112 mm. of mercury had been developed.

The cell was broken and the fractured edges of the wall were examined. These showed a distinct line of cleavage running parallel with the longitudinal axis of the cup and about midway between the two surfaces. Except where the two layers met, the wall seemed dense and free from air-blisters.

The cause of the above-mentioned defect in the moulding of the cup is not certainly known, but it is believed to be due to the use of an excess of clay at the top of the cell. If the interior diameter of the cup were left too small by the preliminary shaping with the fingers, the descending plunger might carry some of this excess of clay before it until the bottom was reached. By further advancement of the plunger this superfluous clay would be forced upward under great pressure and spread over the clay which formed the original wall and from which in the meantime, the water had been partially absorbed by the plaster of Paris. The final effect would, therefore, be the formation of a wall consisting of two layers which under the circumstances could hardly be expected to form a homogeneous whole.

With the hope of preventing the formation of this double layer, the mould has been somewhat modified, but as no cups have been formed in it since the changes were made the benefits to be derived are as yet only a matter of conjecture.

Cup III. — This cup, like cups I. and II., was of Delaware clay without admixture of quartz, feldspar or other clays, and its treatment preliminary to heating was similar to that recorded for the two cups just mentioned.

The dehydration was accomplished in an electric furnace which differed from the one described on pages 35–36 only in minor details, and which had been calibrated by Dr. Frazer.

In the burning of this cup the current was gradually raised

during the course of four days three and one-half hours, from 2.4 to 6.94 amperes. The last reading was as follows: current, 6.94 amperes; electromotive force, 46.0 volts; resistance, 6.63 ohms; temperature calculated from resistance, 833°; electrical energy consumed in the furnace, 319.24 joules; temperature calculated from disappearing electrical energy, 885°.

This cell was burned with cell II. in the gas furnace at a maximum temperature of 1310°. Length of cell upon removal from the electric furnace, 3.62 inches. Length of cell upon removal from gas furnace, 3.34 inches. Shrinkage of cell in gas furnace 7.7 per cent.

This cell was found to be cracked in several places and was unfit for further tests.

Cup IV. — This cup was of English Ball clay without admixture of other materials. It was dried in the usual manner before being introduced into the electric furnace.

The initial current was 1.2 amperes. Three days two and one-half hours were consumed in reaching the highest temperature of the furnace, viz., 851°.

Some of the observations which were made on the dehydra-

TABLE XIII.

Time.	Amperes.	Volts.	Ohms.	Joules.	Temperature Found.	Temp. from Electrical Energy Consumed.
3 : 40 p. m.	4.3	19.5	4.53	83.85	390°	422°
3 : 50 "	4.3	19.7	4.58	84.71	398	424
4 : 00 "	4.3	19.8	4.60	85.14	402	425
4 : 30 "	4.3	20.0	4.65	86.00	410	427
5 : 05 "	4.3	20.2	4.70	86.86	418	430
10 : 10 a. m.	4.3	20.4	4.74	87.72	427	431
10 : 30 "	4.4	21.2	4.82	93.28	442	445
11 : 00 "	4.5	22.0	4.89	99.00	453	460
11 : 20 "	4.5	22.15	4.92	99.67	459	461

tion of this cell between 400° and 460° are presented in Table XIII. It will be noticed that for a current of 4.3 amperes, the maximum difference between the temperature calculated from the resistance of the furnace and the electrical energy

consumed in it, is gradually diminished from 32° to 4°. It is to be borne in mind, however, that not all of the energy represented by these differences, particularly in the first case, is consumed in expelling the water of the clay in the condition of vapor. A portion of it is spent in raising the temperature of the furnace.

During the first part of the cooling of the furnace the temperature was reduced 0.05 ampere at a time, at the rate of 0.4 ampere per hour. At the end of twenty-five hours the circuit was broken. Length of cell before heating, 3.59 inches. Length of cell after heating, 3.56 inches. Shrinkage of cell in electric furnace, 0.8 per cent.

Upon careful examination the cup was found to be cracked and hence was not burned in the gas furnace. It has been found that even extremely minute cracks are a fatal defect in porous vessels which are employed in the investigation of osmotic pressure. For this reason all the cups were examined internally with great care by the aid of a small electric lamp.

Cup V. — Each of the cups previously described had consisted of only a single variety of clay. It was now determined to try the effect of mixing three different clays. Accordingly equal parts by weight of Peach, Delaware; Edgar, Florida; and English Ball clays were very thoroughly mixed and a portion of the material thus prepared was used for cup V., which was dried at a temperature of 40° in a large air-bath provided with a stirrer which kept the air in constant circulation.

Before placing the cup in the electric furnace it was very carefully examined on the interior as well as on the exterior, but no cracks were to be found.

The initial current was 1.4 amperes. During two and one-sixth days the current was slowly increased to 6.6 amperes and was maintained at this point for the succeeding eighteen hours. From the last reading recorded at the time the following data are taken: current, 6.6 amperes; electromotive force, 43.9 volts; resistance, 6.65 ohms; temperature calculated from re-

sistance, 838° ; electrical energy consumed in furnace, 289.74 joules ; temperature calculated from energy consumed, 851°.

The current was decreased 0.05 ampere at a time, at a rate not exceeding 0.2 ampere per hour until it stood at 5.5 amperes. The total time occupied in reducing the current to zero was twenty-seven hours. Length of air-dried cell, 3.59 inches. Length of cell upon removal from electric furnace, 3.55 inches. Shrinkage of cell in electric furnace. 1.1 per cent.

Externally the cell appeared to be quite perfect, but an examination of the interior surface revealed the presence of a crack more than 2 cm. in length. When burned in the kiln of D. F. Haynes & Son this cell was reduced in length to 3.14 inches and the crack, as was anticipated, increased in size.

Total shrinkage in cell, 12.5 per cent. The cell wall showed the same unsatisfactory structure which was mentioned in the description of cup II., viz., a distinct line of cleavage running parallel with the longitudinal axis and about half way between the two surfaces.

Cup VI. — The composition of this cup was the same as that of cup V., viz., a mixture of equal parts of Delaware, Florida and English Ball clays. It was, however, not moulded under high pressure, but was shaped to the mould with the fingers. Like the cup last described, it was dried in the air-bath before being heated in the electric furnace.

The highest current used in dehydrating the clay of which this cup was composed was 6.75 amperes, but the voltage was not read for any current above 6.6 amperes. The maximum temperature, therefore, to which the furnace was raised is unknown. For the current of 6.6 amperes the electromotive force was 43.4 volts. The following data are based upon these readings : resistance, 6.58 ohms ; temperature calculated from resistance, 822° ; electrical energy consumed in furnace, 286.44 joules ; temperature calculated from disappearing electrical energy, 847°.

The current was raised rather more rapidly than usual during

the last part of the heating, and to this fact is undoubtedly to be attributed the large difference between the temperatures calculated by the two methods.

When the furnace was left for the night at 10 p. m.,the current was 6.7 amperes. At ten o'clock the next morning, when the current began to be reduced, it had fallen to 6.4 amperes. Twenty-seven hours later the circuit was broken. Although this cell contained a small crack it was further burned together with cup V. in the kiln of D. F. Haynes & Son. In this case also, the crack was considerably increased in size by this further heating.

Length of air-dried cell, 3.62 inches; on removal from electric furnace, 3.57 inches; on removal from pottery kiln, 3.19 inches. Shrinkage of cell in electric furnace, 1.4 per cent. Total shrinkage, 11.9 per cent.

The appearance of the fractured edges of this cup, when broken, was more unsatisfactory than that of the cups which were moulded under high pressure. Minute cavities were abundant, thus showing that pressure cannot safely be dispensed with in the moulding of the cups.

Cup VII.—A mixture of unknown composition obtained from D. F. Haynes & Son, and called by them "semi-porcelain mixture" was used in the preparation of this cup. It was dried in the air at ordinary temperatures and then introduced into the electric furnace.

The initial current used was less than two amperes. Three and a quarter days were required to reach the maximum current of 9.1 amperes. Owing to unsteadiness of current, the ammeter and voltmeter could not be read with the usual accuracy at the maximum temperature of the furnace. The errors which were as a consequence introduced into the calculation of the resistance, were greatly increased by the necessity of extrapolation, owing to the fact that since making some repairs in the furnace, due to the fusion of one of the platinum wires, it had not been calibrated for temperatures above 904°.

The following data are based upon the last reliable readings of ammeter and voltmeter, viz., current, 9.1 amperes; electromotive force, 77.1 volts. Resistance, 8.47 ohms; temperature calculated from resistance, 1200°; electrical energy consumed in furnace, 770.77 joules. In all probability, the resistance did not rise more than a few hundredths of an ohm above 8.5 ohms.

It should further be stated that in addition to the unfortunate circumstances already mentioned, an accident occurred when the temperature of the furnace was between 800° and 900° which must have occasioned a rather rapid lowering of the temperature for an unknown time and to an unknown degree. It was, therefore, not surprising to find, upon removal of the cup from the furnace, that it contained numerous cracks. It was also completely converted into porcelain. The outside of the cup was covered with glistening particles somewhat resembling frost and the inside of the smaller clay cylinder surrounding the wired portion of the furnace had the same appearance. There can be little doubt that the formation of these particles was due to the volatilization of the platinum or some impurity contained in it. Length of air-dried cell, 3.66 inches. Length of cell, after the burning in electric furnace, 3.35 inches. Shrinkage of cell in electric furnace, 8.4 per cent.

The "semi-porcelain mixture" seems to be quite unfit for use in the construction of cups suitable for the measurement of osmotic pressure, owing to the relatively low temperature at which it fuses.

Cup VIII. — The composition of this cup was the same as that of cups V. and VI., viz., equal parts of Delaware, Florida, and English Ball clays. It was dried in the air at a temperature not above 40° before being introduced into the electric furnace.

Since the burning of this cup was unsatisfactory, owing to an accident, details will not be given. The highest temperature of the furnace was about 865°. The cell was badly

cracked but the texture of the wall, as far as freedom from blisters, channels, etc., was concerned, was excellent.

Cup IX. — This cup was composed of the semi-porcelain mixture used in the formation of cup VII. It was not burned in the electric furnace but was buried in sand and heated probably to about 1100° in the gas furnace. No Seger cones were used and as one or two of the burners were defective, it is possible that the temperature was lower than that mentioned above. The maximum temperature of the furnace was maintained for about seventeen hours. Six and one-half hours after the process of cooling was begun the gas was shut off.

Upon removal from the furnace the cup was found to contain a crack near the bottom. It was porous and fairly strong. Length 3.52 inches.

When an attempt was made to deposit a membrane of copper ferrocyanide in the cup, phenomena similar to those which had been previously noticed in the case of very porous vessels immediately appeared. The current rose rapidly and the liquid in the cell soon became turbid with a precipitate of the ferrocyanide of copper. To each liter of the tenth normal potassium salt used in this experiment, 10 cc. of acetic acid had been added. The second attempt to deposit the same membrane, using a neutral solution of the potassium ferrocyanide, resulted also in failure. As soon as the electromotive force was raised to 50 volts, the current began to rise rapidly and even when the voltage was kept below 30, the same effect was produced to a smaller extent. For instance, in the course of an hour, with an electromotive force varying from 28 to 29 volts, the resistance decreased from 1,812 to 1,439 ohms.

The cell was set up with a half normal solution of sugar, but the membrane exhibited no osmotic pressure.

Cup X. — The mixture used for this cup consisted of clay, feldspar and flint in the following proportions: 55.35 per cent. of equal parts by weight of Delaware, Florida, and English Ball clays; 31.25 per cent. flint; 13.39 per cent. feldspar.

The cup was moulded under pressure and dried for ten days at the temperature of the room, in a cylinder made of plaster of Paris. Previous experience had shown that the evaporation of the water used in mixing the clay was so slow and uniform under these conditions that the cracking which was very apt to take place during the desiccation in air was almost wholly prevented.

The cylinder containing the cup was then placed for a time in the air-bath, which was kept at a temperature of 50°. The cup was buried in sand and burned in the gas furnace to a temperature of 1310°. The maximum temperature of the furnace was maintained for about seven and one-half hours. Total time of heating, forty-eight hours.

Upon opening the furnace the sand was found to be baked so hard that it was necessary to dig it out with a knife. The cup was cracked in several places and had passed over into porcelain. The shrinkage was not determined, owing to the breaking of the cup in an attempt to remove the sand which filled it.

While the foregoing experiments do not, taken by themselves, appear to contribute very largely to the solution of the very difficult problem which is under investigation in this laboratory, they are to be considered as a necessary part of the work which must be accomplished before the obstacles which present themselves in this field are successfully overcome.

BIOGRAPHY.

The writer was born in Kiantone, New York, on October 21, 1873. His early education was obtained in the schools of Jamestown, New York. In 1896 he was graduated from Amherst College with the degree of Bachelor of Arts. Since October, 1899, with the exception of a year spent in teaching chemistry at Cornell University, he has pursued graduate studies in chemistry at the Johns Hopkins University. In 1903–1904 he held a fellowship in chemistry. His subordinate subjects have been physical chemistry and geology.